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TRANSMITTAL LETTER TO THE UNITED STATES PATENT & TRADEMARK OFFICE ATTORNEYS DOCKET NUMBER 50734

DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371

U.S. APPLICATION NO. (If known, see 37 CFR 1.5)

INTERNATIONAL APPLICATION NO. INTERNATIONAL FILING DATE PRIORITY DATE CLAIMED
PCT/EP00/09076 16 September 2000 20 September 1999

TITLE OF INVENTION. METAL COMPLEXES AS CATALYST FOR THE POLYMERIZATION OF UNSATURATED COMPOUNDS

APPLICANT(S) FOR DO/EO/US Andrei GONIOUKH, Marc Oliver KRISTEN, Wolfgang MICKLITZ, Benno BILDSTEIN,
Christoph AMORT

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following
items and other information:

1. /X/ This is a FIRST submission of items concerning a filing under 35 U.S.C. 371
 2. / / This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.
 3. /X/ This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1)
 4. /X/ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
 5. /X/ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. /X/ is transmitted herewith (required only if not transmitted by the International Bureau).
 - b. / / has been transmitted by the International Bureau
 - c. / / is not required, as the application was filed in the United States Receiving Office (RO/USO)
 6. /X/ A translation of the International Application into English (35 U.S.C. 371(c)(2))
 7. /X / Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
 - a. /X / are transmitted herewith (required only if not transmitted by the International Bureau)
 - b. / / have been transmitted by the International Bureau.
 - c. / / have not been made; however, the time limit for making such amendments has NOT expired.
 - d. / / have not been made and will not be made
 8. /X / A translation of the amendments to the claims under PCT Article 19(35 U.S.C. 371(c)(3)).
 9. /X / An oath or declaration of the inventor(s)(35 U.S.C. 171(c)(4))
 10. / / A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).
- Items 11 to 16 below concern other document(s) or information included
11. / / An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
 12. /X/ An assignment document for recording A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included
 13. /X / A FIRST preliminary amendment
/ / A SECOND or SUBSEQUENT preliminary amendment
 14. / / A substitute specification.
 15. / / A change of power of attorney and/or address letter.
 16. /X / Other items or information.
International Search Report
International Preliminary Examination Report

U.S. Appl. No. (If Known) INTERNATIONAL APPLN. NO.
PCT/EP00/09076ATTORNEY'S DOCKET NO.
50734

	CALCULATIONS	PTO USE ONLY
17. /X/ The following fees are submitted		
BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)) Search Report has been prepared by the EPO or JPO.....	\$890.00	
International preliminary examination fee paid to USPTO (37 CFR 1.482).....	\$710.00	
No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2)).....	\$740.00	
Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO	\$1,040.00	
International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied pro visions of PCT Article 33(2)-(4).....	\$100.00	
ENTER APPROPRIATE BASIC FEE AMOUNT = \$ 890.00		
Surcharge of \$130.00 for furnishing the oath or declaration later than 1/20/30 months from the earliest claimed priority date (37 CFR 1.492(e))		
Claims	Number Filed	Number Extra
Total Claims	14	-20
Indep. Claims	1	-3
Multiple dependent claim(s) (if applicable)		
TOTAL OF ABOVE CALCULATION		= 890.
Reduction of 1/2 for filing by small entity, if applicable Verified Small Entity statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28)		
SUBTOTAL		= 890
Processing fee of \$130. for furnishing the English translation later than 1/20/30 months from the earliest claimed priority date (37 CFR 1.492(f))		
TOTAL NATIONAL FEE		= 890.
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) \$40.00 per property		
TOTAL FEES ENCLOSED		= \$ 930.00
Amount to be refunded. \$		
Charged \$		

a./X/ A check in the amount of \$ 930.00 to cover the above fees is enclosed.

b./I/ Please charge my Deposit Account No. _____ in the amount of \$ _____ to cover the above fees. A duplicate copy of this sheet is enclosed.

c./X/ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 11-0345. A duplicate copy of this sheet is enclosed.**NOTE:** Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.SEND ALL CORRESPONDENCE TO:
KEIL & WEINKAUF
1101 Connecticut Ave., N.W.
Washington, D. C. 20036

SIGNATURE

Herbert B. Keil

NAME

Registration No. 18,967

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the Application of)
GONIOUKH et al.) BOX PCT
)
International Application)
PCT/EP 00/09076)
)
Filed: September 15, 2000)
)

For: METAL COMPLEXES AS CATALYSTS FOR THE POLYMERIZATION OF
UNSATURATED COMPOUNDS

PRELIMINARY AMENDMENT

Honorable Commissioner of
Patents and Trademarks
Washington, D.C. 20231

Sir:

Prior to examination, kindly amend the above-identified application as follows:

IN THE CLAIMS

Kindly cancel claims 1-14 and insert new claims 15-28 as shown on the attached
sheets.


REMARKS

The claims were amended in the preliminary examination. New claims 15-28 eliminate
multiple dependency and place them in better form for U.S. filing. No new matter is included.

Favorable action is solicited.

Respectfully submitted,

KEIL & WEINKAUF

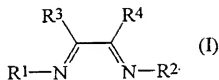

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NEW CLAIMS 15-28

--15. A 1,2-diimine of the formula (I),



where the symbols have the following meanings:

R¹ is a radical of the formula NR⁵R⁶,

R² is a radical of the formula NR⁵R⁶ or an alkyl, aryl or cycloalkyl radical,

R⁵ and R⁶ together with the N atom form a 5-, 6- or 7-membered ring in which one or more of the -CH- or -CH₂- groups may be replaced by appropriate heteroatom groups and which may be saturated or unsaturated and unsubstituted, substituted or fused with further carbocyclic or heterocyclic 5- or 6-membered rings which may in turn be saturated or unsaturated or substituted or unsubstituted,

and

R³, R⁴ are, independently of one another, H or alkyl, aryl or cycloalkyl radicals

or

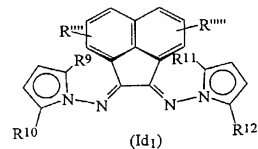
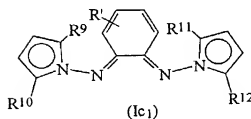
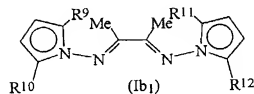
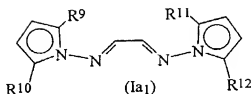
R³ and R⁴ together with the two imine carbon atoms form a carbocyclic or heterocyclic 5- to 8-membered ring which may be saturated or unsaturated and unsubstituted, substituted or fused with further carbocyclic or heterocyclic 5- or 6-

membered rings which may in turn be saturated or unsaturated and substituted or unsubstituted.

16. A compound as claimed in claim 1, wherein the radicals of the formula NR⁵R⁶ are pyrrole radicals or radicals derived from pyrrole, where one or more -CH- groups in the pyrrole ring may be replaced by nitrogen, which may be unsubstituted, substituted or fused with further carbocyclic or heterocyclic 5- or 6-membered rings which may in turn be saturated or unsaturated and substituted or unsubstituted.

17. A compound as claimed in claim 2, wherein the pyrrole radicals or radicals derived from pyrrole are substituted in the 2 and 5 positions by C1-C6-alkyl groups, which may be linear, branched or substituted by heteroatoms, and/or aryl groups which may be unsubstituted or in turn substituted by C1-C6-alkyl groups which may be heteroatom-substituted.

18. A compound as claimed in claim 3 which has one of the formulae (Ia₁), (Ib₁), (Ic₁) or (Id₁):



where R₉, R₁₀, R₁₁ and R₁₂ are, independently of one another, C1-C6-alkyl radicals

and

R', R''', R'''' are H or alkyl, cycloalkyl or aryl.

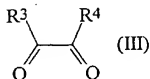
19. A process for preparing symmetrical compounds of the formula (I) as claimed in claim 1 in which $R_1 = R_2$ by reacting compounds of the formula (II)



where

R_5 and R_6 together with the N atom form a 5-, 6- or 7-membered ring in which one or more of the $-CH-$ or $-CH_2-$ groups may be replaced by appropriate heteroatom groups and which may be saturated or unsaturated and unsubstituted, substituted or fused with further carbocyclic or heterocyclic 5- or 6-membered rings which may in turn be saturated or unsaturated or substituted or unsubstituted,

with 1,2-diketo compounds of the formula (III),



where

R^3, R^4 are, independently of one another, H or alkyl, cycloalkyl or aryl radicals,

or

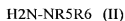
R^3 and R^4 together with the two carbonyl carbon atoms form a carbocyclic or heterocyclic 5- to 8-membered ring which may be saturated or unsaturated and unsubstituted, substituted or fused with further carbocyclic or heterocyclic

5- or 6-membered rings which may in turn be saturated or unsaturated and substituted or unsubstituted,

in a single-stage process under acidic reaction conditions in alcoholic solution or in the presence of a trialkylaluminum catalyst in an aprotic solvent in a ratio of the compound of the formula (II) to the compound of the formula (III) of 2:0.7-1.3.

20. A process for preparing unsymmetrical compounds of the formula (I) as claimed in claim 1 in which $R_1 \neq R_2$ in a two-stage process in which:

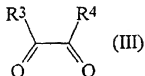
a) compounds of the formula (II)



where

R_5 and R_6 together with the N atom form a 5- or 6-membered ring in which one or more of the $-CH-$ or $-CH_2-$ groups may be replaced by appropriate heteroatom groups and which may be saturated or unsaturated and unsubstituted, substituted or fused with further carbocyclic or heterocyclic 5- or 6- membered rings which may in turn be saturated or unsaturated or substituted or unsubstituted,

are reacted in a first step with 1,2-diketo compounds of the formula (III)



where

R3, R4 are, independently of one another, H or alkyl, aryl or cycloalkyl radicals

or

5

R3 and R4 together with the two carbonyl carbon atoms form a carbocyclic or heterocyclic 5- to 8-membered ring which may be saturated or unsaturated and unsubstituted, substituted or fused with further carbocyclic or heterocyclic 5- or 6-membered rings which may in turn be saturated or unsaturated and substituted or unsubstituted,

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in a ratio of the compounds of the formula (II) to the compounds of the formula (III) of 1:0.8-1.2 under acidic conditions in alcoholic solution to form the corresponding monoimine and the solvent is subsequently removed under reduced pressure,

and

20

b) the monoimine is reacted in a second step with compounds of the formula (II) which are different from the compounds of the formula (II) used in step a), or with compounds of the formula (IV)

25



where R7 and R8 are, independently of one another, alkyl, aryl or cycloalkyl radicals, or

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with amines of the formula (V)



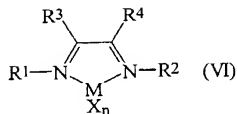
where

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R13 is an alkyl radical, an aryl radical or a cycloalkyl radical,

in an aprotic solvent, in the presence of a trialkylaluminum catalyst, in a ratio of the monoimine to a compound of the formula (II) of the formula (IV) or (V) of 1:0.8-1.2.

21. A compound of the formula (VI),



where the symbols having the following meanings:

R¹ is a radical of the formula NR⁵R⁶,

R² is a radical of the formula NR⁵R⁶ or an alkyl, aryl or cycloalkyl radical,

R⁵ and R⁶ together with the N atom form a 5-, 6- or 7-membered ring in which one or more of the -CH- or -CH₂- groups may be replaced by appropriate heteroatom groups and which may be saturated or unsaturated and unsubstituted, substituted or fused with further carbocyclic or heterocyclic 5- or 6-membered rings which may in turn be saturated or unsaturated or substituted or unsubstituted,

and

R³, R⁴ are, independently of one another, H or alkyl, aryl or cycloalkyl radicals

or

- 5 R3 and R4 together with the two imine carbon atoms form a carbocyclic or heterocyclic 5- to 8-membered ring which may be saturated or unsaturated and unsubstituted, substituted or fused with further carbocyclic or heterocyclic 5- or 6-membered rings which may in turn be saturated or unsaturated and substituted or unsubstituted;
- 10 M is a transition metal of group 8, 9 or 10 of the Periodic Table of the Elements,
- and
- X is a halide or a C1-C6-alkyl radical;
- 15 n is the valence of the metal M.
22. A compound as claimed in claim 7, wherein M = Pd or Ni and n = 2 or 3.
- 20 23. A process for preparing compounds of the formula (VI) as claimed in claim 7 by reacting corresponding compounds of the formula (I) with salts of transition metals of groups 8, 9 and 10 of the Periodic Table of the Elements.
- 25 24. A process for preparing polyolefins by polymerization of unsaturated compounds in the presence of an activator and a compound of the formula (VI) as claimed in claim 7 as catalyst.
- 30 25. A process as claimed in claim 11, wherein the catalyst is present in homogeneous form in solution or in heterogeneous form immobilized on a support in the polymerization.
26. A process as claimed in claim 11, wherein methylaluminoxane or N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate is used as activator.

27. A process as claimed in claim 11, wherein an unsaturated compound or a combination of unsaturated compounds selected from among ethylene, C3-C20-monoolefins, cycloolefins and propylene is used.
- 5 28. A polyolefin which can be prepared by a process as claimed in claim 11.--

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AS ORIGINALLY FILED

**Metal complexes as catalysts for the
 polymerization of unsaturated compounds**

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The present invention relates to 1,2-diimine compounds, a process for preparing them, catalysts having 1,2-diimine ligands, a process for preparing them and their use in the polymerization of unsaturated compounds.

15

There is great interest in the development of novel families of catalysts for the polymerization of unsaturated compounds in order to obtain better control over the properties of polyolefins or further novel products.

20

The use of transition metal catalysts containing late transition metals (in particular transition metals of groups 7, 8, 9 and 10 of the Periodic Table of the Elements) is of particular interest because of their ability to tolerate heteroatom functionalities. However, a disadvantage is that the transition metal catalysts containing late transition metals frequently tend, in contrast to transition metal catalysts containing early transition metals (in particular transition metals of transition groups III to V of the Periodic Table of the Elements), to result in dimerization or oligomerization of unsaturated compounds because of competing β -hydride elimination.

25

Transition metal catalysts containing late transition metals which are suitable for the polymerization of unsaturated compounds are known from the prior art.

30

V.C. Gilbson et al., Chem. Commun. 1998, 849-850, and M. Brookhart et al., J. Am. Chem. Soc. 1998, 120, 4049-4050, disclose new olefin polymerization catalysts based on Fe(II) and Co(II). These catalysts have 2,6-bis(imino)pyridyl ligands which are aryl-substituted on the iminonitrogen atoms and display high activities in the polymerization of ethylene. The polyethylene obtained is essentially linear and the molecular weight is strongly dependent on the substituents on the aryl radical.

35

H. tom Dieck, Z. Naturforsch. 1981, 36b, 823-832, describes bis(diazadiene)nickel(0) complexes having aromatic substituents on the nitrogen

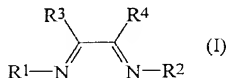
atom and also describes their confirmations as a function of the substituents on the aromatic radical.

- 5 M. Brookhart et al., J. Am. Chem. Soc. 1995, 117, 6415-6415, describe catalysts based on Pd(II) and Ni(II) for the polymerization of ethylene and α -olefins. These catalysts contain 1,2-diimine ligands and in the polymerization of ethylene and α -olefins give polymers having a high molecular weight. Depending on the ligand system, the metal, the temperature and the pressure, the branching of polyethylene prepared using these catalysts can be adjusted from strongly branched to only
- 10 slightly branched. According to M. Brookhart et al., J. Am. Chem. Soc. 1996, 118, 267-268, the copolymerization of ethylene and propylene with functionalized vinyl monomers is also possible using these catalysts with Pd(II) as metal.

- WO 96/23010 relates to processes for the polymerization and copolymerization of
- 15 olefins such as ethylene, acrylic olefins and others. Catalysts used are transition metal compounds containing metals of the group Ti, Zr, Sc, V, Cr, rare earth metals, Se, Co, Ni and Pd. Ligand systems disclosed are diimine ligand systems, in particular 1,2-diimine ligand systems.

- 20 It is an object of the present invention to provide a novel catalyst containing a transition metal of group 8, 9, or 10 of the Period Table of the Elements (late transition metal) as central metal for the polymerization of unsaturated compounds. This object may be subdivided into the provision of a ligand system for this catalyst and a process for preparing this ligand system and the provision of a
- 25 process for preparing the corresponding catalyst.

We have found that this object is achieved by 1,2-diimines of the formula (I),



30

where the symbols have the following meanings:

R¹ is a radical of the formula NR₅R₆,

R2 is a radical of the formula NR₅R₆ or an alkyl, aryl or cycloalkyl radical,

5 R₅ and R₆ together with the N atom form a 5-, 6- or 7-membered ring in which one or more of the -CH- or -CH₂- groups may be replaced by appropriate heteroatom groups and which may be saturated or unsaturated and unsubstituted, substituted or fused with further carbocyclic or heterocyclic 5- or 6- membered rings which may in turn be saturated or unsaturated or substituted or unsubstituted,

10 and

RR, R₄ are, independently of one another, H or alkyl, aryl or cycloalkyl radicals
15 or

20 R₃ and R₄ together with the two imine carbon atoms form a carbocyclic or heterocyclic 5- to 8-membered ring which may be saturated or unsaturated and unsubstituted, substituted or fused with further carbocyclic or heterocyclic 5- or 6-membered rings which may in turn be saturated or unsaturated and substituted or unsubstituted.

25 The 1,2-diimines of the present invention have at least one nitrogen-nitrogen bond between at least one of the two imine nitrogen atoms and at least the radical R₁.

30 These compounds are useful, in particular, as ligand systems for preparing novel, efficient catalyst systems for the polymerization or copolymerization of unsaturated compounds. These novel ligands are easy to prepare and make it possible for the radicals to be varied within a wide range. This system is therefore very flexible and allows ligands and complexes to be tailored to various applications.

35 In the description above and in the following, alkyl radicals are linear or branched C₁-C₂₀-alkyl radicals in general, preferably C₁-C₁₀-alkyl radicals, particularly preferably C₁-C₈-alkyl radicals. These alkyl radicals may contain heteroatoms.

Examples of suitable alkyl radicals are methyl, i-propyl, t-butyl, trifluoromethyl and trimethylsilyl radicals.

For the purposes of the present invention, aryl radicals are unsubstituted and substituted C6-C20-aryl radicals in general, preferably C6-C14-aryl radicals which may be monosubstituted or polysubstituted, very particularly preferably C6-C10-aryl radicals substituted by C1-C6-alkyl radicals, for example 4-methylphenyl, 2,6-dimethylphenyl, 2,6-diethylphenyl, 2,6-diisopropylphenyl, 2-tert-butylphenyl, 2,6-di(tert-butyl)phenyl or 2-i-propyl-6-methylphenyl. The aryl radicals may also be substituted by heteroatoms, e.g. by F.

For the purposes of the present invention, cycloalkyl radicals are C5-C8-cycloalkyl radicals in general (the number of carbon atoms refers to the number of carbon atoms in the cycloalkyl ring) which may be unsubstituted or monosubstituted or polysubstituted by alkyl or aryl radicals. Preference is given to C5- and C6-cycloalkyl radicals.

According to the present invention, R5 and R6 together with the N atom may form a 5- or 6-membered ring in which one or more of the -CH- or -CH2- groups may be replaced by suitable heteroatom groups. Preferred heteroatom groups are -N- or -NH- groups. Particular preference is given to from 0 to 3 -CH- or -CH2- groups being replaced by -N- or -NH- groups.

The 5-, 6- or 7-membered ring can be saturated or unsaturated. In the case of an unsaturated ring, the ring may be monounsaturated or polyunsaturated. Preference is given to unsaturated 5-membered rings. Unsaturated rings also include, in the case of the 5-membered rings, aromatic rings such as unsubstituted or substituted pyrrole radicals, which are particularly preferred.

The 5-, 6- or 7-membered ring may be unsubstituted, substituted or fused with further carbocyclic or heterocyclic 5- or 6-membered rings which may in turn be saturated or unsaturated and substituted or unsubstituted.

For the purposes of the present invention, carbocyclic rings are rings which have a pure carbon. In the heterocyclic rings, one or more -CH2- or -CH- groups are replaced by heteroatoms, preferably -NH- or -N- groups. Particular preference is given to heterocyclic rings having a nitro atom in the ring system.

Possible substituents in these carbocyclic and heterocyclic 5- or 6-membered rings are the abovementioned alkyl, aryl or cycloalkyl radicals. The rings can be monosubstituted or polysubstituted. Monosubstitution to trisubstitution is preferred. The ring system can also be ortho- or ortho- and peri-fused. The system is preferably ortho-fused; particular preference is given to one 1 or 2 phenyl radicals being fused to the central 5- or 6-membered ring, for example indole, carbazole or derivatives thereof.

- 10 In a particularly preferred embodiment, the ring is 5-membered. Very particular preference is given to an unfused 5-membered ring, in particular a pyrrole radical or a radical derived from pyrrole where zero, one or more, preferably from 0 to 3, particularly preferably 0 or 2, -CH- groups in the pyrrole ring may be replaced by nitrogen. Examples are the pyrrole system and the triazole system. Particular
- 15 preference is given to pyrrole radicals or radicals derived from pyrrole which are substituted in the 2 and 5 positions by C1-C6-alkyl groups, which may be linear, branched or substituted by heteroatoms, and/or aryl groups which may be unsubstituted or in turn substituted by C1-C6-alkyl groups which may be substituted by heteroatoms. Preferred substituents in the 2 and 5 positions of the
- 20 pyrrole ring are methyl, i-propyl, t-butyl, phenyl and substituted aryl radicals as defined above.

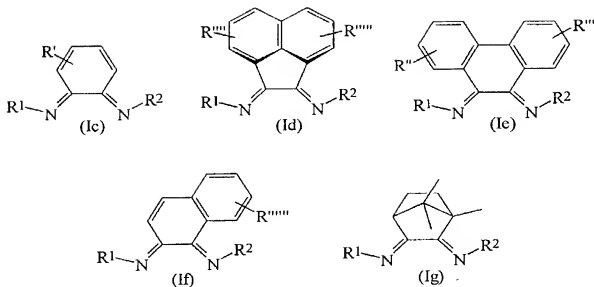
According to the present invention, R3 and R4 in the formula (I) can be, independently of one another, H or alkyl, aryl or cycloalkyl radicals, with preferred

25 radicals being as defined above, or can together with the two imine carbon atoms form a carbocyclic or heterocyclic 5- to 8-membered ring, preferably a 5- to 6-membered ring, which may be saturated or unsaturated and unsubstituted, substituted or fused with further carbocyclic or heterocyclic 5- or 6-membered rings which may in turn be saturated or unsaturated and substituted or

30 unsubstituted.

Preferably, R3 and R4 = H (Ia) or methyl (Ib) or together with the imine carbon atoms form a ring, resulting in structures of the formulae (Ic) to (Ig):

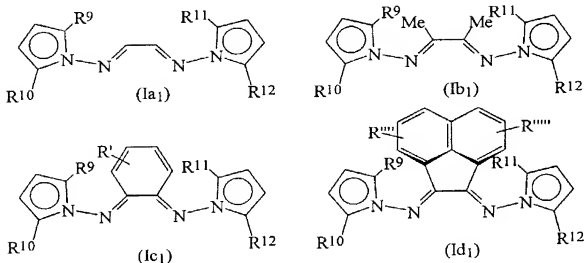
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where R' , R'' , R''' , R'''' , R''''' , R'''''' = H, alkyl, cycloalkyl or aryl, as defined above,

or are trifluoromethyl (Ih), phenyl (Ii) or furfuryl (Ij).

Particular preference is given to compounds of the formula (I) in which R_1 , R_2 , R_3 and R_4 have the meanings indicated in the formulae (Ia₁), (Ib₁), (Ic₁) and (Id₁):

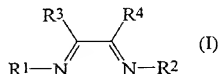


where R_9 , R_{10} , R_{11} and R_{12} are, independently of one another, C₁-C₂₀-alkyl radicals which may be linear or branched, preferably C₁-C₁₀-alkyl radicals, particularly preferably C₁-C₈-alkyl radicals. These alkyl radicals may be

heteroatom-substituted. Examples of suitable alkyl radicals are methyl, i-propyl, t-butyl, trifluoromethyl and trimethylsilyl radicals.

The radicals R', R'', R''' are H or alkyl, aryl or cycloalkyl radicals, as defined above.

The novel 1,2-diimines of the formula (I)



10

where

R¹ is a radical of the formula NR⁵R⁶,

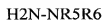
15 R² is a radical of the formula NR⁵R⁶ or an alkyl, aryl or cycloalkyl radical,

and the other symbols are as defined above, are generally prepared by condensation of the corresponding amino compounds with 1,2-diketo compounds.

20 They can be synthesized readily and it is possible to synthesize a large number of different compounds of the formula (I) in good yields.

The preferred method of preparation depends on the desired 1,2-diimine. In the following, preferred embodiments for the preparation of symmetrical 1,2-diimines in which R¹ = R² = NR⁵R⁶ and unsymmetrical diimines in which R¹ ≠ R² and R² is a radical of the formula NR⁵R⁶ which is different from R¹ or an alkyl, aryl or cycloalkyl radical are described.

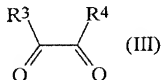
25 In a preferred embodiment, symmetrical 1,2-diimines of the formula (I) in which R¹ = R² are prepared by reacting compounds of the formula (II)



where

R5 and R6 are as defined above,

5 with 1,2-diketo compounds of the formula (III),



where

10 R3, R4 are as defined above.

The process is carried out in a single stage under acidic reaction conditions, preferably with addition of an acid, particularly preferably formic acid, in alcoholic solution, preferably in methanol. Alternatively, the process can be carried out in the presence of a trialkylaluminum, preferably trimethylaluminum, as catalyst in an aprotic solvent, preferably in toluene. The ratio of the compound of the formula (II) to the compound of the formula (III) is 2:0.7-1.3, preferably 2:0.9-1.1, particularly preferably 2:1. The reaction is preferably carried out under acidic conditions in methanol/formic acid. The ratio of methanol to formic acid is generally from 1:1 to 1:5, preferably from 1:1 to 1:3.

In general, the condensation is carried out at from 0 to 100°C, preferably from 15 to 80°C, particularly preferably from 20 to 40°C. The reaction time is generally from 20 minutes to 48 hours, preferably from 1 hour to 16 hours, particularly preferably from 2 hours to 14 hours. The precise reaction conditions depend on the compounds used in each case. If the compounds of the general formulae (II) and (III) bear particularly bulky radicals and condense only slowly to form the desired 1,2-diimines, it may be preferable to carry out the reaction in the presence of a trialkylaluminum catalyst in aprotic solvents.

30 In a further preferred embodiment, the unsymmetrical 1,2-diimines of the formula (I) in which R1 ≠ R2 are prepared in a two-stage process in which:

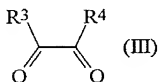
a) compounds of the formula (II)

H₂N-NR₅R₆ (II)

where

R₅ and R₆ are as defined above,

are reacted in a first step with 1,2-diketo compounds of the formula (III)



where

R₃, R₄ are as defined above,

in a ratio of the compounds of the formula (II) to the compounds of the formula (III) of 1:0.8-1.2, preferably 1:0.9-1.1, particularly preferably 1:1, under acidic conditions, preferably with addition of acids, particularly preferably formic acid, in alcoholic solution, preferably in methanol, to form the corresponding monoimine and the solvent is subsequently removed under reduced pressure,

and

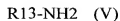
b) the monoimine is reacted in a second step with compounds of the formula (I) which are different from the compounds of the formula (II) used in step a), or

with compounds of the formula (IV)

H₂N-NR₇R₈ (IV)

where R₇ and R₈ are, independently of one another, alkyl, aryl or cycloalkyl radicals, or

with amines of the formula (V)



5 where

R13 is an alkyl radical, an aryl radical or a cycloalkyl radical, as defined above,

10 in an aprotic solvent, preferably in toluene, in the presence of a trialkylaluminum catalyst, preferably using trimethylaluminum as catalyst, in a ratio of the monoimine to a compound of the formula (II) of the formula (IV) or (V) of 1:0.8-1.2, preferably 1:0.9-1.1, particularly preferably 1:1.

15 In general, the condensation in step a) is carried out at from 0 to 100°C, preferably from 15 to 80°C, particularly preferably from 20 to 40°C. The reaction time is generally from 20 minutes to 48 hours, preferably from 1 hour to 16 hours, particularly preferably from 2 hours to 14 hours. The precise reaction conditions
20 depend on the compounds used in each case. Step b) is generally carried out at from 0 to 100°C, preferably from 20 to 80°C, particularly preferably from 30 to 60°C. The reaction time is generally from 20 minutes to 48 hours, preferably from 1 hour to 16 hours, particularly preferably from 2 hours to 7 hours. The precise reaction conditions again depend on the compounds used in each case.

25 As compounds of the formula (II)



30 where

R5 and R6 are as defined above,

35 preference is given to using compounds in which the group NR5R6 is a pyrrole radical or a radical derived from pyrrole which is very particularly preferably substituted in the 2 and 5 positions by C1-C6-alkyl groups, which may be linear, branched and substituted by heteroatoms, and/or aryl groups which may be

unsubstituted or in turn substituted by C1-C6-alkyl groups which may be heteroatom-substituted. Preferred substituents in the 2 and 5 positions of the pyrrole ring are methyl, i-propyl, t-butyl, phenyl or substituted aryl radicals, as defined above.

5

Such N-aminopyrroles can be obtained, for example, by the following two-stage process:

- 10 i) Reaction of a suitable 1,2-diketone with an equivalent amount of acetylhydrazine or benzoyloxycarbonylhydrazine in the presence of a catalytic amount of acid, preferably p-toluenesulfonic acid, in an inert organic solvent, preferably toluene, to form the corresponding acetyl- or benzoyloxycarbonyl-protected N-aminopyrrole; and
- 15 ii) Hydrolysis of the protected N-aminopyrrole with an excess of base, preferably potassium hydroxide, in a high-boiling inert organic solvent, preferably ethylene glycol, to give the corresponding free N-aminopyrrole.

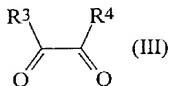
The subsequent work-up is carried out in a customary manner.

20

Figure 1 shows, by way of example, the synthesis of 2,5-disubstituted N-aminopyrroles.

1,2-Diketo compounds used in the process of the present invention are compounds of the formula (III):

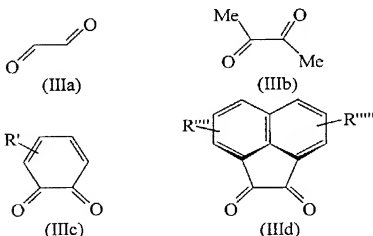
25



where R³ and R⁴ are as defined above. Preferred 1,2-diketo compounds are glyoxal (IIIa), butane-2,3-dione (IIIb), general aromatic ortho-quinones (IIIc), acenaphthenequinone and derivatives thereof (IIId), phenanthrenequinone and derivatives thereof (IIIe), 1,2(β)-naphthoquinone and derivatives thereof (IIIf), camphorquinone (+/-, 1R, 1S) (IIIg) and also 1,1,1,4,4,4-hexafluoro butane-2,3-

30

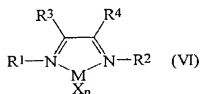
dione (IIIh), benzil (IIIi) and furil (IIIj). Particular preference is given to using carbonyl compounds of the formulae (IIIa), (IIIb), (IIIc) and (IIId),



5

where R' , R'''' , $R''''' = H$, alkyl or aryl, as defined above.

The compounds of the present invention are useful as ligands for catalysts which can be used for the polymerization of unsaturated compounds. The compounds of the present invention are particularly useful as ligands for catalysts containing a late transition metal, i.e. a metal of group 8, 9 or 10 of the Periodic Table of the Elements. The present invention therefore also provides compounds of the formula (VI),



15

where the symbols having the following meanings:

R_1 is a radical of the formula NR_5R_6 ,

20

R_2 is a radical of the formula NR_5R_6 or an alkyl, aryl or cycloalkyl radical,

R_5 and R_6 together with the N atom form a 5-, 6- or 7-membered ring in which one or more of the $-CH-$ or $-CH_2-$ groups may be replaced by

25

appropriate heteroatom groups and which may be saturated or unsaturated and unsubstituted, substituted or fused with further carbocyclic or heterocyclic 5- or 6- membered rings which may in turn be saturated or unsaturated or substituted or unsubstituted,

5

and

RR, R4 are, independently of one another, H or alkyl, aryl or cycloalkyl radicals

10

or

R3 and R4 together with the two imine carbon atoms form a carbocyclic or heterocyclic 5- to 8-membered ring which may be saturated or unsaturated and unsubstituted, substituted or fused with further carbocyclic or heterocyclic 5- or 6-membered rings which may in turn be saturated or unsaturated and substituted or unsubstituted;

15

M is a transition metal of group 8, 9 or 10 of the Periodic Table of the Elements,

20

and

X is a halide or a C1-C6-alkyl radical;

25

n is the valence of the metal M, preferably 2 or 3.

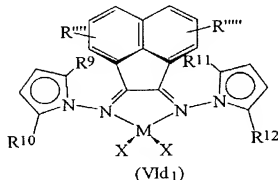
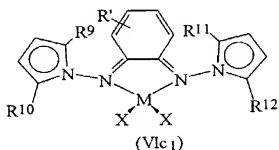
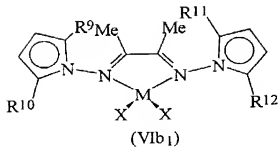
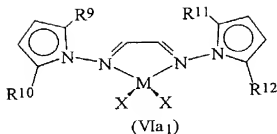
The transition metal M of group 8, 9 or 10 of the Periodic Table of the Elements is preferably Pd, Co, Ni or Fe. Particular preference is given to Pd and Ni. The ligands X can be, independently of one another, halides or alkyl radicals. They are preferably chloride, bromide or methyl radicals. As the group MX₂, particular preference is given to PdCl₂, Pd(Cl)CH₃, NiCl₂ or NiBr₂.

30

Preferred radicals R1, R2, R3 and R4 are as defined above.

35

Very particular preference is given to compounds of the formulae (VIa) and (VIb):



where R', R''', R'''' = H, alkyl, cycloalkyl or aryl, as defined above, and

- 5 R₉, R₁₀, R₁₁ and R₁₂ are, independently of one another, C₁-C₂₀-alkyl radicals, preferably C₁-C₁₀-alkyl radicals, particularly preferably C₁-C₈-alkyl radicals, which may be linear or branched and may be heteroatom-substituted, for example methyl, i-propyl, t-butyl, trifluoromethyl or trimethylsilyl radicals,

10

and

MX₂ is PdCl₂, Pd(Cl)CH₃, NiCl₂, CoCl₂, NiBr₂ or FeCl₂, particularly preferably NiBr₂ or PdCl₂.

15

After activation by means of an activator (cocatalyst), these complexes are very active in the polymerization of unsaturated compounds. They can be obtained easily and can be prepared in a wide range of variants. Thus, the present invention provides a very variable system which can be tailored to the particular application.

20

The novel compounds of the formula (V) are usually prepared by reacting corresponding compounds of the formula (I) with salts of transition metals of groups 8, 9 and 10 of the Periodic Table of the Elements.

In a preferred embodiment, a compound of the formula (I) which is suitable as ligand is combined in an organic solvent, e.g. tetrahydrofuran (THF) or methylene chloride, with an appropriate metal salt, e.g. $\text{NiCl}_2(\text{DME})$ (DME = 1,2-dimethoxyethane), $\text{NiBr}_2(\text{DME})_2$, CoCl_2 , $\text{PdCl}_2(\text{benzonitrile})_2$, $\text{PdClMe}(\text{COD})$ (COD = 1,5-cyclooctadiene). The molar ratio of ligand to metal salt is generally from 1.5:1 to 1:1.5, preferably from 1.2:1 to 1:1.2, particularly preferably about 1:1. The reaction mixture is generally stirred at temperatures from room temperature to 50°C , preferably from room temperature to 40°C , particularly preferably at room temperature, for generally from 0.5 hour to 16 hours, preferably from 1 to 6 hours, particularly preferably from 1 to 3 hours. The work-up is carried out in a customary manner, e.g. by removal of the solvent under reduced pressure, washing of the residue with a solvent in which the residue (product) is largely insoluble, e.g. with diethyl ether, if desired digestion in a nonpolar solvent, e.g. hexane, filtration, washing and drying.

Figure 2 and Figure 3 show, by way of example, the synthesis of selected novel ligands of the formula (I) and the synthesis of selected metal complexes prepared therefrom.

The novel metal complexes of the formula (VI) can be obtained easily and are suitable as catalysts for the polymerization of unsaturated compounds. They display a surprisingly high productivity in the polymerization or copolymerization of unsaturated compounds.

The present invention therefore also provides for the use of compounds of the formula (VI) as catalysts in a process for the polymerization of unsaturated compounds and provides a process for preparing polyolefins by polymerization of unsaturated compounds in the presence of the catalyst according to the present invention and an activator.

It is known that the structure of polymers and thus their properties and applications depend on the catalyst used in the polymerization and on the reaction conditions during the polymerization. The catalysts of the present invention thus offer an opportunity of preparing novel polymers having specific property profiles.

Suitable activators (cocatalysts) are, in particular, strong, uncharged Lewis acids, ionic compounds having Lewis acid cations and ionic compounds containing Brönsted acids as cations.

- 5 As strong, uncharged Lewis acids, preference is given to compounds of the formula (VII),



- 10 where the symbols have the following meanings:

M' is an element of main group III of the Periodic Table of the Elements, preferably B, Al or Ga, particularly preferably B,

- 15 X₁, X₂, X₃ are, independently of one another, hydrogen, C₁-C₁₀-alkyl, C₆-C₁₅-aryl, alkylaryl, arylalkyl, haloalkyl or haloaryl, each having from 1 to 10 carbon atoms in the alkyl radical and from 6 to 20 carbon atoms in the aryl radical, or fluoride, chloride, bromide or iodide, preferably haloaryl, particularly preferably pentafluorophenyl.

- 20 Very particular preference is given to compounds of the formula (VII) in which X₁, X₂ and X₃ are identical, preferably tris(pentafluorophenyl)borane.

- A further preferred uncharged Lewis acid used as activator (cocatalyst) is
25 "R₁₄AlO" (alkylaluminoxane), where R₁₄ is a C₁-C₂₅-alkyl radical, preferably a C₁-C₄-alkyl radical, particularly preferably a methyl radical (methylaluminoxane).

Suitable ionic compounds having Lewis acid cations are compounds of the formula (VIII),

- 30
$$[(Y a^+)Q_1Q_2 \dots Q_z]d^+ \quad (VIII)$$

where the symbols having the following meanings:

- 35 Y is an element of main group I to VI or of transition group I to VIII of the Periodic Table of the Elements,

- Q1 to Qz are singly negatively charged groups such as C1-C28-alkyl, C6-C15-aryl, alkylaryl, arylalkyl, haloalkyl, haloaryl, each having from 6 to 20 carbon atoms in the aryl radical and from 1 to 28 carbon atoms in the alkyl radical, C1-C10-cycloalkyl which may bear C1-C10-alkyl groups as substituents, halide, C1-C28-alkoxy, C6-C15-aryloxy, silyl or mercaptyl groups,
- a is an integer from 1 to 6,
- z is an integer from 0 to 5,
- d is the difference a-z, but d is greater than or equal to 1.

Particularly useful Lewis-acid cations are carbonium cations, oxonium cations and sulfonium cations and also cationic transition metal complexes. Particular mention may be made of the triphenylmethyl cation, the silver cation and the 1,1'-dimethylferrocenyl cation. They preferably have noncoordinating counterions, in particular boron compounds as are also mentioned in WO 91/09882, preferably tetrakis(pentafluorophenyl)borate.

Ionic compounds containing Brønsted acids as cations and preferably likewise noncoordinating counterions are likewise mentioned in WO 91/09882, the preferred cation is N,N-dimethylanilinium.

The amount of activator is preferably from 0.1 to 10 equivalents, based on the catalyst (VI). In the case of alkylaluminoxanes, in particular methylaluminoxane, the amount of activator is generally from 50 to 1000 equivalents, preferably from 100 to 500 equivalents, particularly preferably from 100 to 300 equivalents, based on the catalyst (VI).

The polymerization process of the present invention is suitable for preparing homopolymers or copolymers. Preference is given to using unsaturated compounds or combinations of unsaturated compounds selected from the group consisting of ethylene, C3-C20-monoolefins, ethylene and C3-C20-monoolefins, cycloolefins, cycloolefins and ethylene and cycloolefins and propylene. Preferred cycloolefins are norbornene, norbornadiene and cyclopentene.

The abovementioned monomers can be copolymerized with monomers in which a carbonyl group is present, for example esters, carboxylic acids, carbon monoxide and vinyl ketones. Preference is given to the following combinations of unsaturated compounds: ethylene and C3-C20-monoolefins, ethylene and an alkyl acrylate, in particular methyl acrylate, ethylene and an acrylic acid, ethylene and carbon monoxide, ethylene, carbon monoxide and an acrylate ester or an acrylic acid, in particular methyl acrylate, and also propylene and alkyl acrylate, in particular methyl acrylate.

Depending on the reaction conditions and the monomers used, it is possible to obtain homopolymers, random copolymers or block copolymers by means of the process of the present invention.

The polymerization is carried out under generally customary conditions in solution, e.g. as a high-pressure polymerization in a high-pressure reactor or high-pressure autoclave, in suspension or in the gas phase (e.g. gas-phase fluidized-bed polymerization process). Preference is given to a polymerization in solution. The corresponding polymerization processes can be carried out as batch processes, semicontinuously or continuously, using procedures known from the prior art.

The catalyst systems of the present invention can be used in the form of unsupported catalysts or supported catalysts, depending on the polymerization conditions.

In a solution polymerization, the catalyst systems of the present invention are homogeneously dissolved in the solution. In this case, the catalysts of the formula (VI) can be prepared in situ and used directly, without prior isolation, in the polymerization.

As support materials, preference is given to using finely divided solids whose particle diameters are generally in the range from 1 to 200 μm , preferably from 30 to 70 μm .

Examples of suitable support materials are silica gels, preferably ones of the formula $\text{SiO}_2 \cdot a \text{Al}_2\text{O}_3$, where a is in the range from 0 to 2, preferably from 0 to 0.5; these are thus aluminosilicates or silicon dioxide. Such products are

commercially available, for example Silica Gel 332 from Grace or ES 70x from Crosfield.

- 5 To remove adsorbed water, the support materials can be subjected to a thermal or chemical treatment or be calcined. Preference is given to a treatment at from 80 to 200°C, particularly preferably from 100 to 150°C.

Other inorganic compounds such as Al_2O_3 or $MgCl_2$ or mixtures of these can likewise be used as support materials.

10

The catalysts can also be prepared in situ in the presence of support materials.

- 15 Particularly suitable solvents are aprotic organic solvents. The catalyst system, the monomer or monomers and the polymer may be soluble or insoluble in these solvents, but the solvents should not participate in the polymerization. Useful solvents are alkanes, cycloalkanes, selected halogenated hydrocarbons and aromatic hydrocarbons. Preferred solvents are hexane, toluene and benzene, particularly preferably toluene.

- 20 The polymerization temperatures in the solution polymerization are generally in the range from -20 to 350°C, preferably from 0 to 350°C, particularly preferably from +20 to 100°C, very particularly preferably from room temperature to 80°C. The reaction pressure is generally from 0.1 to 3000 bar, preferably from 0.1 to 2000 bar, particularly preferably from 1 to 200 bar, very particularly preferably
25 from 5 to 40 bar. The polymerization can be carried out in any apparatus suitable for the polymerization of unsaturated compounds.

- To control the molecular weight of the polymers, the polymerization can be carried out in the presence of hydrogen gas which acts as chain transfer reagent. Usually,
30 the higher the hydrogen concentration, the lower the mean molecular weight.

Moreover, further auxiliaries customary in the respective polymerization process can be used.

- 35 The polymerization process of the present invention opens up a route to polyolefins having novel structures and properties. The present invention therefore

also provides polymers which can be prepared by the process of the present invention.

The following examples illustrate the invention.

5

Examples

(The numbering of the example compounds is independent of the numbering of the compounds in the description.)

10

The syntheses of the ligands and complexes were carried out in the absence of air and moisture. The apparatuses and reagents used were prepared appropriately.

A Synthesis of 2,5-disubstituted N-aminopyrroles

15

Example 1:

General procedure for the synthesis of benzoyloxycarbonyl-protected 2,5-disubstituted N-aminopyrroles 2a-d (Figure 1)

20

4-8 g of the 1,4-diketones 1a-d were refluxed together with one equivalent of benzoyloxycarbonylhydrazine and a catalytic amount of p-toluenesulfonic acid in 80 ml of toluene. After 18 hours, the solution was cooled and the solvent was taken off under reduced pressure. The white crystalline residues were pulverized and refluxed in a suitable solvent mixture (THF/hexane 1:4 or CHCl₃/ hexane 1:5) so as to give a saturated solution from which the compounds 2a-d then crystallized on cooling. These were filtered off and dried in a high vacuum.

25

Preparative and analytical data for the benzoyloxycarbonyl-protected 2,5-disubstituted N-aminopyrroles:

30

Compound 2a:

Yield: 85%, C₁₄H₁₆N₂O₂, M.p.: 104-108°C, ¹H NMR (CDCl₃): δ 1.97 (s 6H methyl), 5.11 (s 2H CH₂C₆H₆), 5.67 (s 2H pyrrole), 7.26 (s 5H phenyl); MS: M⁺ = 224.5 m/e.

35

Compound 2b:

Yield: 88.6%, C₁₈H₂₄N₂O₂, M.p.: 118-121°C, ¹H NMR (CDCl₃): δ 1.18 (d 12H methyl), 2.75 (m 2H CH(CH₃)₂), 5.20 (pd 2H CH₂C₆H₆), 5.84 (2H pyrrole), 7.3 (m 5H phenyl); MS: M⁺ = 166.5 m/e.

Compound 2c:

Yield: 78.1%, C₂₀H₂₈N₂O₂, M.p.: 155-158°C, ¹H NMR (CDCl₃): δ 1.25/1.33 (18H t-butyl), 5.24/5.15 (pd 2H CH₂C₆H₆), 5.82/5.79 (pd 2H pyrrole), 7.28 (s 1H NH), 7.4 (m 5H phenyl); MS: M⁺ = 328 m/e.

Compound 2d:

Yield: 84.2%, C₂₄H₂₀N₂O₂, M.p.: 194-197°C, ¹H NMR (CDCl₃): δ 5.04/5.1 (pseudo d 2H CH₂C₆H₆), 6.46 (s 2H pyrrole), 7.01 (s 1H NH), 7.1-7.5 (m 15H phenyl); MS: M⁺ = 368.5 m/e.

Example 2:

20

General procedure for selective removal of the benzoyloxycarbonyl protective group, synthesis of the aminopyrroles 3a-d (Figure 1):

5-15 g of the protected pyrrole 2a-d were heated at 180°C with 5 equivalents of KOH in absolute dihydroxyethane (15-50 ml). After one hour, the solution was allowed to cool, a little water (4-10 ml) was added and the pyrroles 3a-d were crystallized at -5°C. the white crystalline compounds were filtered off, washed twice with water and dried in a high vacuum.

30 Preparative and analytical data for the 2,5-disubstituted N-aminopyrroles:

Compound 3a:

Yield: 80.0%, C₆H₁₁N₂, M.p.: 40-45°C, ¹H NMR (CDCl₃): δ 2.10 (s 6H methyl), 5.59 (s 2H pyrrole); MS: M⁺ = 234.5 m/e.

Compound 3b:

Yield: 95.4%, C₁₀H₁₈N₂, M.p.: 56-57°C, ¹H NMR (CDCl₃): δ 1.25 (d 12H methyl), 3.05 (m 2H CH(CH₃)₂), 5.73 (2H pyrrole); MS: M⁺ = 166.5 m/e.

5 Compound 3c:

Yield: 89.6%, C₁₂H₂₂N₂, M.p.: 66-68°C, ¹H NMR (CDCl₃): δ 1.38 (s 18H t-butyl), 4.40 (s 2H NH₂), 5.73 (s 2H pyrrole); MS: M⁺ = 194.5 m/e.

10 Compound 3d:

Yield: 89.5%, C₁₆H₁₄N₂, M.p.: 217-219°C, ¹H NMR (CDCl₃): δ 4.69 (s 2H NH₂), 6.18 (s 2H pyrrole), 7.1-7.6 (m 15H phenyl); MS: M⁺ = 194.5 m/e.

15 **B Synthesis of the asymmetrically and symmetrically substituted diimine ligands 4, 5, 6, 10**

Example 3:

20 Synthesis of the symmetrically substituted diimine ligands 4, 5 (Figure 2)

1-2 g of an aminopyrrole 3a or 3b and 0.5 equivalent of a diketone (acenaphthenequinone or 2,3-butanedione) were stirred for 12 hours in a 2:1 mixture of methanol/formic acid (total: 5 ml). After a short time, the solutions
 25 became light yellow or red. The reaction solutions were slowly diluted with a little water, stirred for another 1 hour and then filtered. The solid was washed with water and then dried in a high vacuum.

Preparative and analytical data for the symmetrically substituted diimine ligands
 30 4a, b and 5a, b:

Compound 4a:

Yield: 82%, C₁₆H₂₂N₄, M.p.: 108-112°C, ¹H NMR (CDCl₃): δ 2.10 (s 6H methylpyrrole), 2.23 (s 6H diketone methyl), 5.94 (s 2H pyrrole); MS: M⁺ = 270 m/e.

Compound 4b:

Yield: 74.5%, C₂₄H₃₈N₄, M.p.: 101-104°C, ¹H NMR (CDCl₃): δ 1.18 (d 6H CH(CH₃), 2.16 (s 6H diketone methyl), 2.59 (m 4H CH(CH₃)), 5.94 (s 2H pyrrole); MS: M⁺ = 382.5 m/e.

Compound 5a:

Yield: 72.6%, C₂₄H₂₂N₄, ¹H NMR (CDCl₃): δ 1.98 (s 12H methylpyrrole), 5.93 (s 2H pyrrole), 6.67 (d 2H), 7.41 (t 2H), 7.92 (d 2H) acenaphthenequinone; MS: M⁺ = 366.5 m/e.

The synthesis of the compound 5b was carried out under virtually the same conditions as described above. The only differences were that a 1:3 solvent mixture of methanol/formic acid was used for the reaction and the reaction mixture was refluxed for 12 hours.

Compound 5b:

Yield: 74.8%, C₃₂H₃₈N₄, M.p.: 254-256°C, ¹H NMR (CDCl₃): δ 4.13 (dxd 24H CH(CH₃), 2.75 (m 4H CH(CH₃)) 6.06 (s 2H pyrrole), 6.67 (d 2H), 7.54 (t 2H), 7.98 (d 2H) acenaphthenequinone; MS: M⁺ = 382.5 m/e.

Example 4:

Synthesis of the asymmetrically substituted diimine ligands 6a, b (Figure 2)

The synthesis of the asymmetrically substituted ligands was carried out in two steps. The diketone was firstly condensed with one amine component under acidic conditions and then with the second component under anhydrous conditions using trimethylaluminum as auxiliary reagent.

100-300 mg of the aminopyrroles 3b and d were refluxed with one equivalent of acenaphthenequinone in methanol/ formic acid 1:3 for 12 hours. The solvent was then taken off in a high vacuum so as to leave the completely acid-free monoimine. All further reaction steps were carried out under argon using dry solvents.

A solution of activated 2,6-diisopropylaniline was prepared by carefully stirring 15.0 ml of 2,6-diisopropylaniline in dry toluene and 40.0 ml of 2.0 M trimethylaluminum in toluene at room temperature. The solution was heated at 60°C until gas evolution abated. After cooling, the solution was diluted with toluene to a total volume of 100 ml; the resulting standard solution had a molarity of 0.80 and was stored in a refrigerator. Two equivalents of this solution were then added to the monoimines prepared above. The red solutions were stirred at 50°C for 5 hours. After cooling, the solutions were carefully hydrolyzed with 30% strength aqueous sodium hydroxide. The aqueous phase was extracted twice with methylene chloride, the organic phase was dried over sodium sulfate and the solvent was removed under reduced pressure. The crude products were purified by recrystallization from a mixture of chloroform/hexane.

Preparative and analytical data for the asymmetrically substituted diimine ligands 6a, b:

Compound 6a:

Yield: 60.1%, C₃₄H₃₉N₃, M.p.: 274-276°C, ¹H NMR (CDCl₃): δ 0.94 0.96 1.02 1.05 1.19 1.21 1.22 1.23 (2xdxd 24H CH(CH₃) phenyl and pyrrole), 2.76 2.97 (m 4H CH(CH₃) phenyl and pyrrole), 6.04 (s 2H pyrrole), 6.57 6.59 6.60 6.63 (2xd 2H), 7.34 7.50 (2xt 2H), 7.86 7.89 7.94 7.96 (2xd 2H) acenaphthenequinone; MS: M⁺ = 489.5 m/e.

Compound 6b:

Yield: 65.1%, C₄₀H₃₅N₃, M.p.: 260-270°C, ¹H NMR (CDCl₃): δ 0.85 0.88 1.29 1.31 (dxd 24H CH(CH₃) pyrrole), 2.95 (m 4H CH(CH₃) pyrrole), 6.69 (s 2H pyrrole), 6.48 6.50 6.69 6.72 (2xd 2H), 7.44 7.30 (2xt 2H), 7.71 7.74 7.80 7.83 (2xd 2H) acenaphthenequinone, 7.0-7.3(m 10H diphenylpyrrole; MS: M⁺ = 557.5 m/e.

Example 5: Synthesis of the symmetrically substituted diimine ligands 10 (Figure 3)

To synthesize the compounds 10b, c (Figure 3), the amino components (2-5 g of N-aminopiperidine and N-aminocarbazole) were dissolved in 20 ml of dry toluene and, under an argon atmosphere, one equivalent of trimethylaluminum (2.0 M solution in toluene) was added. These solutions were refluxed for 3 hours (10b) or heated at 60°C (10c) until gas evolution abated. After cooling to room temperature, 0.25 equivalent of acenaphthenequinone was added, resulting in the solutions immediately turning red. After 4 hours at 50°C, 100 ml of ether and 200 ml of 20% strength aqueous KOH solution were carefully added, the mixtures were shaken well and the organic phases were separated off. These were then dried over sodium sulfate and the solvent was taken off under reduced pressure. The red residues were recrystallized from toluene/hexane.

Compound 10b:

Yield: 58.7%, C₂₂H₂₆N₄, ¹H NMR (CDCl₃): δ 1.4-1.7 (m 12H), 3.4 (t 6H piperidine -NCH₂-), 7.62 (m 2H) 8.22 (d 2H) 8.26 (d 2H) acenaphthenequinone; MS: M⁺ = 346 m/e.

Compound 10c:

Yield: 47.6%, C₃₆H₂₂N₄, ¹H NMR (CDCl₃): δ 6.8-7.5 (m 14H), 7.7-8.2 (m 4H) 8.2-8.4 (m 4H); MS: M⁺ = 510.5 m/e.

5

C Synthesis of the nickel complexes

Example 6:

10 General procedure for the synthesis of the nickel bromide complexes (Figure 2, 3)

50-200 mg of the compounds 4a, 5a, 5b, 6a, 6b and 10b were stirred under argon with one equivalent of NiBr₂*DME or NiCl₂*DME in dry methylene chloride (20-80 ml) for at least 15 hours. After only a few minutes, the solutions became brown to black and the complex formed was usually precipitated as a brown solid. 15 The solvent was taken off in a high vacuum, the brown residue was finely pulverized and digested a number of times with dry hexane (30 ml). The hexane phase could easily be removed by decantation; the products 7a, 8a, 9b, 9a and 11b were dried in a high vacuum.

20

The nickel complex 8b could not be isolated in the manner described above, but instead had to be used together with the reaction solution in the polymerization experiments.

25 Preparative and analytical data for the nickel complexes:

Compound 7a:

Yield: 58.3%, C₁₆H₂₂N₄Br₂Ni, brown powder.

30

Compound 8a:

Yield: 60.1%, C₂₄H₂₂N₄Br₂Ni, brown powder.

35 Compound 9a:

Yield: 84.2%, C₃₄H₃₉N₃Br₂Ni, brown powder.

Compound 9b:

Yield: 44.6%, $C_{40}H_{35}N_3Br_2Ni$, brown powder.

5

Compound 11b: Yield: 66.6%, $C_{22}H_{26}N_4Cl_2Ni$, black powder, NMR (d_6 DMSO), paramagnetic, δ 2.5 (s broad 4H), 2.75 (s broad 8H), 3.95 (s broad 8H), 8.6-9.2 (m 6H) acenaphthenequinone; MS: $M^+ = 476.5$ m/e.

10 For chemical reaction schemes and structures, see Appendix 1

D Polymerization experiments

Example 7:

15

Homopolymerization of ethene using catalysts which have been isolated

250 ml of dry toluene are placed in a 500 ml four-neck glass flask. After addition of 28.9 mmol of MAO (methylaluminoxane) and 289 μ mol of catalyst 9a, ethene is blown through the solution under atmospheric pressure at a flow rate of 40 l/h. A polymerization temperature of 50-55°C is set. After 4.5 hours, the polymerization is stopped by addition of HCl/MeOH.

The polymerization mixture is separated in a separating funnel. The toluene phase is washed with H₂O and dried. After filtration through a column filled with aluminum oxide (neutral), the polymer is isolated by evaporation of the toluene (75°C, 0.1 mbar, 3 h).

The polymerization experiments using the catalysts 7a, 8a and 9b were carried out analogously. Specific details are shown in Table 1.

The polymerization results and structure analyses of the polymers are summarized in Table 2.

35 Example 8:

Homopolymerization of ethene using a catalyst prepared in situ

250 ml of toluene are placed in a 500 ml four-neck glass flask. After addition of 14.3 mmol of MAO (methylaluminoxane) and 143 μ mol of a mixture of ligand 5b and NiBr₂-DME complex in methylene chloride which had been stirred overnight
5 at 22°C, ethene is blown through the solution at atmospheric pressure at a flow rate of 40 l/h. The polymerization temperature is set to 50-55°C. After 4.5 hours, the polymerization is stopped by addition of HCl/MeOH.

The polymerization mixture is separated in a separating funnel. The toluene phase
10 is washed with H₂O and dried. After filtration through a column filled with aluminum oxide (neutral), the polymer is isolated by evaporation of the toluene (75°C, 0.1 mbar, 3 h).

The polymerization results and structure analysis are summarized in Table 2.

Example 9:

Homopolymerization of ethene using $[((Ar)N=C(An)-C(An)=N(Ar))NiBr_2]$ (Ar: 2,6-diisopropylphenyl, An: acenaphthene) as catalyst (Comparative Example 1)
 5 (M. Brookhart et al., J. Am. Chem. Soc. 1995, 117, 6415-6415)

250 ml of dry toluene are placed in a 500 ml four-neck glass flask. After addition of 16 mmol of MAO and 160 μ mol of $[((Ar)N=C(An)-C(An)=N(Ar))NiBr_2]$, ethene is blown through the solution at atmospheric pressure at a flow rate of
 10 40 l/h. The polymerization temperature is set to 50-55°C. After 4.5 hours, the polymerization is stopped by addition of HCl/MeOH. The mixture is separated in a separating funnel. The toluene phase is washed with H₂O and dried. After filtration through a column filled with aluminum oxide (neutral), the polymer is isolated by evaporation of the toluene (75°C, 0.1 mbar, 3 h).

15 The polymerization results and structure analysis are summarized in Table 2.

The figures below show:

20 Figure 1: Synthesis of 2,5-disubstituted N-aminopyrroles

Figure 2: Synthesis of the ligands 4a, b; 5a, b; 6a, b and the nickel complexes 7a; 8a, b; 9a, b

25 Figure 3: Synthesis of the ligands 10b, c and the nickel complex 11b

Table 1: Polymerizations using nickel catalysts

Catalyst	Comparative Example	9a	8b2	8a	7a	9b
	11					
Catalyst concentration [μmol]	160	289	143	43	51	25.8
Methylaluminoxane (MAO)	1:100	1:100	1:100	1:100	1:100	1:100
Ethene flow rate [L/h]	40	40	40	40	40	40
Solvent	Toluene	Toluene	Toluene	Toluene	Toluene	Toluene
Amount of solvent [ml]	250	250	250	250	250	250
Polymer obtained [g]	14.00	24.95	13.05	5.25	8.50	0.80
Catalyst activity [g PE/ (mmol of cat.)	87.5	86.3	91.3	122.1	166.7	31.0

1 Brookhart catalyst

2 Catalyst used in situ without work-up

1100 900 800 700 600 500 400 300 200 100 0

Table 2: Polymer analysis

Catalyst	Comparative Example 11	9a	8b2	8a	7a	9b
Eta value	2.24	1.5	2.51	0.28	0.21	3.66
GPC analysis	252,698	129,004	208,210	9595	10,452	409,672
Mw [g/mol]						
Mn [g/mol]	90,388	19,399	80,995	3250	3702	26,021
Q	2.8	6.7	2.6	3.0	2.8	15.7
NMR analysis	76.3	70.1	28.3	5.2	10.8	18.8
Methyl groups [CH3/1000 C]						
Ethyl groups [CH3/1000 C]	16.9	12.1	2.8	0.7	1.5	1.6
Propyl groups [CH3/1000 C]	7.2	-	1.7	-	0.8	-
Buryl groups [CH3/1000 C]	7.1	6.0	2.0	-	-	-
Pentyl groups [CH3/1000 C]	4.3	4.6	2.2	1.5	1.5	1.5
C6 and longer [CH3/1000 C]	13.3	13.7	4.0	8.9	7.5	3.0
Total CH3 [CH3/1000 C]	125.1	106.5	41.0	16.3	22.1	24.9
DSC analysis Tg3 [°C]	-62	-62	-29	-	-	-

1 Brookhart catalyst

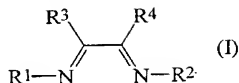
2 Catalyst was used in situ without work-up

3 Glass transition temperature of a sample cooled rapidly from 160°C; sample weight: about 13 mg; heating rate: 20°C/min.

AS ENCLOSED TO IPER

We claim:

- 5 1. A 1,2-diimine of the formula (I),



where the symbols have the following meanings:

10

R1 is a radical of the formula NR5R6,

R2 is a radical of the formula NR5R6 or an alkyl, aryl or cycloalkyl radical,

15

R5 and R6 together with the N atom form a 5-, 6- or 7-membered ring in which one or more of the -CH- or -CH2- groups may be replaced by appropriate heteroatom groups and which may be saturated or unsaturated and unsubstituted, substituted or fused with further carbocyclic or heterocyclic 5- or 6-membered rings which may in turn be saturated or unsaturated or substituted or unsubstituted,

20

and

25

R3 and R4 together with the two imine carbon atoms form a carbocyclic or heterocyclic 5- to 8-membered ring which may be saturated or unsaturated and unsubstituted, substituted or fused with further carbocyclic or heterocyclic 5- or 6-membered rings which may in turn be saturated or unsaturated and substituted or unsubstituted.

30

2. A compound as claimed in claim 1, wherein the radicals of the formula NR5R6 are pyrrole radicals or radicals derived from pyrrole, where one or

more -CH- groups in the pyrrole ring may be replaced by nitrogen, which may be unsubstituted, substituted or fused with further carbocyclic or heterocyclic 5- or 6-membered rings which may in turn be saturated or unsaturated and substituted or unsubstituted.

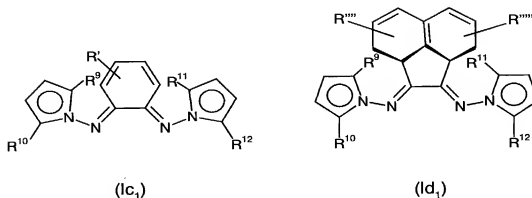
5

3. A compound as claimed in claim 2, wherein the pyrrole radicals or radicals derived from pyrrole are substituted in the 2 and 5 positions by C1-C6-alkyl groups, which may be linear, branched or substituted by heteroatoms, and/or aryl groups which may be unsubstituted or in turn substituted by C1-C6-alkyl groups which may be heteroatom-substituted.

10

4. A compound as claimed in claim 3 which has one of the formulae (Ic1) or (Id1):

15



20

where R9, R10, R11 and R12 are, independently of one another, C1-C6-alkyl radicals

and

25

R', R''', R'''' are H or alkyl, cycloalkyl or aryl.

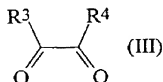
5. A process for preparing symmetrical compounds of the formula (I) as claimed in claim 1 in which R1 = R2 by reacting compounds of the formula (II)

H₂N-NR₅R₆ (II)

where

R₅ and R₆ together with the N atom form a 5-, 6- or 7-membered ring in which one or more of the -CH- or -CH₂- groups may be replaced by appropriate heteroatom groups and which may be saturated or unsaturated and unsubstituted, substituted or fused with further carbocyclic or heterocyclic 5- or 6-membered rings which may in turn be saturated or unsaturated or substituted or unsubstituted,

with 1,2-diketo compounds of the formula (III),



where

R₃ and R₄ together with the two carbonyl carbon atoms form a carbocyclic or heterocyclic 5- to 8-membered ring which may be saturated or unsaturated and unsubstituted, substituted or fused with further carbocyclic or heterocyclic 5- or 6-membered rings which may in turn be saturated or unsaturated and substituted or unsubstituted,

in a single-stage process under acidic reaction conditions in alcoholic solution or in the presence of a trialkylaluminum catalyst in an aprotic solvent in a ratio of the compound of the formula (II) to the compound of the formula (III) of 2:0.7-1:3.

6. A process for preparing unsymmetrical compounds of the formula (I) as claimed in claim 1 in which R₁ ≠ R₂ in a two-stage process in which:

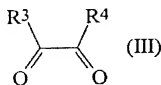
a) compounds of the formula (II)



where

R₅ and R₆ together with the N atom form a 5- or 6-membered ring in which one or more of the -CH- or -CH₂- groups may be replaced by appropriate heteroatom groups and which may be saturated or unsaturated and unsubstituted, substituted or fused with further carbocyclic or heterocyclic 5- or 6- membered rings which may in turn be saturated or unsaturated or substituted or unsubstituted,

are reacted in a first step with 1,2-diketo compounds of the formula (III)



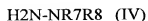
where

R₃ and R₄ together with the two carbonyl carbon atoms form a carbocyclic or heterocyclic 5- to 8-membered ring which may be saturated or unsaturated and unsubstituted, substituted or fused with further carbocyclic or heterocyclic 5- or 6-membered rings which may in turn be saturated or unsaturated and substituted or unsubstituted,

in a ratio of the compounds of the formula (II) to the compounds of the formula (III) of 1:0.8-1.2 under acidic conditions in alcoholic solution to form the corresponding monoimine and the solvent is subsequently removed under reduced pressure,

and

- b) the monoimine is reacted in a second step with compounds of the formula (II) which are different from the compounds of the formula (II) used in step a), or with compounds of the formula (IV)



where R_7 and R_8 are, independently of one another, alkyl, aryl or cycloalkyl radicals, or

with amines of the formula (V)

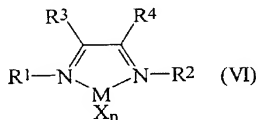


where

R_{13} is an alkyl radical, an aryl radical or a cycloalkyl radical,

in an aprotic solvent, in the presence of a trialkylaluminum catalyst, in a ratio of the monoimine to a compound of the formula (II) of the formula (IV) or (V) of 1:0.8-1.2.

7. A compound of the formula (VI),



where the symbols having the following meanings:

R^1 is a radical of the formula NR_5R_6 ,

R2 is a radical of the formula NR₅R₆ or an alkyl, aryl or cycloalkyl radical,

R5 and R6 together with the N atom form a 5-, 6- or 7-membered ring in which one or more of the -CH- or -CH₂- groups may be replaced by appropriate heteroatom groups and which may be saturated or unsaturated and unsubstituted, substituted or fused with further carbocyclic or heterocyclic 5- or 6-membered rings which may in turn be saturated or unsaturated or substituted or unsubstituted,

and

R3 and R4 together with the two imine carbon atoms form a carbocyclic or heterocyclic 5- to 8-membered ring which may be saturated or unsaturated and unsubstituted, substituted or fused with further carbocyclic or heterocyclic 5- or 6-membered rings which may in turn be saturated or unsaturated and substituted or unsubstituted;

M is a transition metal of group 8, 9 or 10 of the Periodic Table of the Elements,

and

X is a halide or a C₁-C₆-alkyl radical;

n is the valence of the metal M.

8. A compound as claimed in claim 7, wherein M = Pd or Ni and n = 2 or 3.
9. A process for preparing compounds of the formula (VI) as claimed in claim 7 by reacting corresponding compounds of the formula (I) with salts of transition metals of groups 8, 9 and 10 of the Periodic Table of the Elements.

10. The use of a compound of the formula (VI) as claimed in claim 7 as catalyst in a process for the polymerization of unsaturated compounds.
11. A process for preparing polyolefins by polymerization of unsaturated compounds in the presence of an activator and a compound of the formula (VI) as claimed in claim 7 as catalyst.
12. A process as claimed in claim 11, wherein the catalyst is present in homogeneous form in solution or in heterogeneous form immobilized on a support in the polymerization.
13. A process as claimed in claim 11 or 12, wherein methylaluminumoxane or N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate is used as activator.
14. A process as claimed in any of claims 11 to 13, wherein an unsaturated compound* or a combination of unsaturated compounds selected from among ethylene, C3-C20-monoolefins, cycloolefins and propylene is used.

Abstract

1,2-Diimines having at least one nitrogen-containing heterocyclic group bound via a nitrogen atom to at least one of the two imine nitrogen atoms can be used as ligands for preparing metal complexes with transition metals of groups 8, 9 or 10 of the Periodic Table of the Elements which can in turn be used as catalysts for the polymerization of unsaturated compounds. A process for preparing polyolefins by polymerization of unsaturated compounds in the presence of an activator and the metal complex as catalyst is provided.

Key to figures

Note to corrector/finisher:

- 5 In addition, in Figure 1, Ethylenglycol becomes ethylene glycol.

- 1/3 -

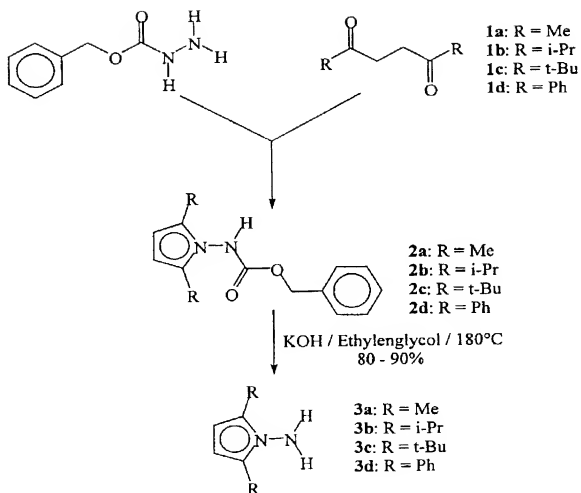


Figure 1

- 2 / 3 -

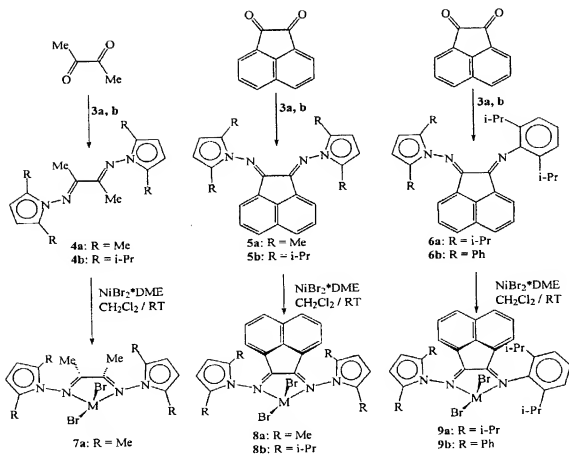


Figure 2

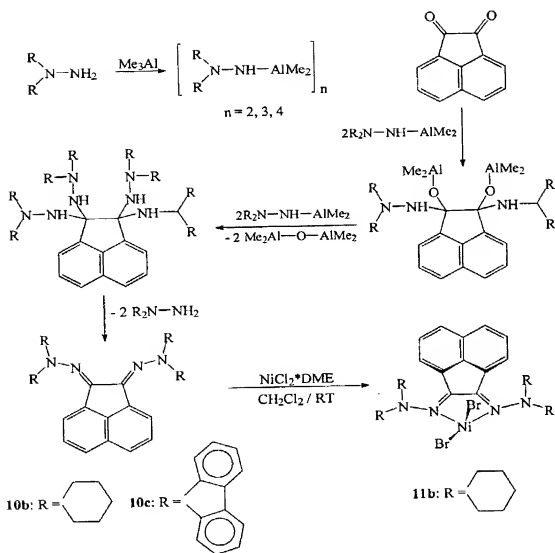


Figure 3

Declaration, Power of Attorney



26474

PATENT & TRADEMARK OFFICE

CUSTOMER No.

Page 1 of 4

0050/050734

We (I), the undersigned inventor(s), hereby declare(s) that:

My residence, post office address and citizenship are as stated below next to my name,

We (I) believe that we are (I am) the original, first, and joint (sole) inventor(s) of the subject matter which is claimed and for which a patent is sought on the invention entitled

Metal complexes as catalyst for the polymerization of unsaturated compounds

the specification of which

☒ is attached hereto.

I | was filed on _____ as

Application Serial No. _____

and amended on _____.

☒ was filed as PCT international application

Number PCT/EP 00/09076

on 15 September 2000

and was amended under PCT Article 19

on _____ (if applicable).

We (I) hereby state that we (I) have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

We (I) acknowledge the duty to disclose information known to be material to the patentability of this application as defined in Section 1.56 of Title 37 Code of Federal Regulations.

We (I) hereby claim foreign priority benefits under 35 U.S.C. § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed. Prior Foreign Application(s)

Application No.

Country

Day/Month/Year

Priority
Claimed

19944993.7

Germany

20 September 1999

☒ Yes ☐ No

Declaration

Page 2 of 4

0050/050734

We (I) hereby claim the benefit under Title 35, United States Codes, § 119(e) of any United States provisional application(s) listed below.

_____	_____
(Application Number)	(Filing Date)
_____	_____
(Application Number)	(Filing Date)

We (I) hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s), or § 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

Application Serial No.	Filing Date	Status (pending, patented, abandoned)
------------------------	-------------	--

_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____

And we (I) hereby appoint Messrs. **HERBERT B. KEIL**, Registration Number 18,967; and **RUSSEL E. WEINKAUF**, Registration Number 18,495; the address of both being Messrs. Keil & Weinkauff, 1101 Connecticut Ave., N.W., Washington, D.C. 20036 (telephone 202-659-0100), our attorneys, with full power of substitution and revocation, to prosecute this application, to make alterations and amendments therein, to sign the drawings, to receive the patent, and to transact all business in the Patent Office connected therewith.

We (I) declare that all statements made herein of our (my) own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Declaration

Page 3 of 4

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